

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-278 750

International Conference on Oxidants, 1976
Analysis of Evidence and Viewpoints
Part V. The Issue of Oxident Transport

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Prepared for

Environmental Sciences Research Lab., Research Triangle Park, N.C.

Nov 77

EPA-600/3-77-117
November 1977

PB 278 750

Ecological Research Series

**INTERNATIONAL CONFERENCE ON OXIDANTS,
1976 - ANALYSIS OF EVIDENCE
AND VIEWPOINTS
Part V. The Issue of Oxidant Transport**



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NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/3-77-117	2.	3. REPORT ACCEPTANCE NO. PB278750
4. TITLE AND SUBTITLE INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS Part V. The Issue of Oxidant Transport	5. REPORT DATE NOVEMBER 1977	
6. PERFORMING ORGANIZATION CODE		8. PERFORMING ORGANIZATION REPORT NO.
7. AUTHOR(S) 1. Donald H. Pack 2. Elmer Robinson 3. Fred Vukovich	10. PROGRAM ELEMENT NO. 1AA603 AJ-13 (FY-76)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS 1. Consulting Meteorologist, McLean, VA 2. Washington State Univ., Pullman, WA 3. Research Triangle Institute, RTP, NC	11. CONTRACT/GRANT NO. 1. DA-7-1935A 2. DA-7-2085A 3. DA-7-2170H	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	13. TYPE OF REPORT AND PERIOD COVERED Final	
14. SPONSORING AGENCY CODE EPA/600/09		15. SUPPLEMENTARY NOTES Partially funded by the Office of Air Quality Planning and Standards.
16. ABSTRACT In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control. Part V includes discussions on the issue of oxidant transport written by Donald H. Pack, Consulting Meteorologist, McLean, Virginia; Elmer Robinson, Washington State University, Pullman, Washington; and Fred M. Vukovich, Research Triangle Institute, Research Triangle Park, North Carolina. The authors deal with the phenomena of urban plume formation and transport, measurement and tracking, and oxidants and precursor ranges, and recommend future studies.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS * Air pollution * Ozone * Transport properties	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group 13B 07B
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 74
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE A04-A01

INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 -
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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

Part V includes discussions on the issue of oxidant transport written by Donald H. Pack, Consulting Meteorologist, McLean, Virginia; Elmer Robinson, Washington State University, Pullman, Washington; and Fred M. Vukovich, Research Triangle Institute, Research Triangle Park, North Carolina. The authors deal with the phenomena of urban plume formation and transport, measurement and tracking, and oxidants and precursor ranges, and recommend future studies.

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ACKNOWLEDGMENTS

These contracts were jointly funded by the Office of Research and Development (Environmental Sciences Research Laboratory) and the Office of Air Quality Planning and Standards.

The assistance of the technical editorial staff of Northrop Services, Inc. (under contract 68-02-2566) in preparing these reports is gratefully acknowledged.

INTRODUCTION

Basil Dimitriadis and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted out by EPA to scientists (who do not work for EPA or industry) with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of oxidant transport. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow.

THE ISSUE OF OXIDANT TRANSPORT

Basil Dimitriades and A. Paul Altshuller

It is to be remembered that this review-analysis effort is concerned only with existing issues, that is with questions that have been answered but conflictingly. If such a definition of issues is to be observed strictly, then while there are numerous unanswered questions there may be no issue related to oxidant transport, at least, none other than those already defined and discussed in connection with the stratospheric ozone and the natural emissions. To explain, one major question relevant to the oxidant problem is on the relative strengths of the natural and the anthropogenic sources in a given region or area. This question has not been answered unequivocally and quantitatively because anthropogenic pollutant transport makes it difficult to assess the strength of the natural sources. The question has been answered qualitatively, a consensus being that pollutant transport does occur and contributes to oxidant buildup in areas far from the sources (2-4). Quantitative answers, however, have not been agreed upon, and this disagreement constitutes the issues already presented in the preceding two sections of this analysis.

Aside from its connection to the natural vs anthropogenic sources question, the phenomenon of oxidant transport is of interest for yet another extremely important reason. This reason is the strong possibility - a fact, to some investigators - that oxidant and/or oxidant precursors transported from upwind sources obscure the role and impact of local emissions to a degree that local control requirements cannot be estimated with confidence. In fact, this obscuring effect is a problem of much broader nature, affecting both main components of the oxidant control strategy, namely:

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- (a) the source-receptor relationship, that is, the geographical definition of the area within which emission control must be applied in order to reduce the oxidant levels observed in a (given) locality, and
- (b) the quantitative relationship between oxidant-related air quality and precursor emission rates.

This connection between oxidant transport and oxidant control strategy is a conclusion arrived at as a result of numerous recent field studies (2-4). Specifically, these studies established that the emission-dispersion and photochemical reaction processes do not have a simple and "local" nature as was assumed in the designing of the first - and current - oxidant control strategy. The phenomena of urban oxidant plume formation and movement, rural oxidant occurrence (at problem levels), "Sunday-weekday effect," and nighttime oxidant occurrence, previously either unnoticed or thought to be "odd," are now believed to be manifestations of an extremely complex emission/pollutant dispersion process. Such complexities, for example, are introduced by horizontal and/or vertical transport of oxidants and/or of precursor mixtures to long distances without excessive dilution.

It is this connection between oxidant control strategy and oxidant transport, and, within this context, the specific areas of nature, extent of, and consequences from pollutant transport, in which several questions exist and need to be answered. Some of these questions have been given conflicting answers, but the supporting evidence was in almost every case either scant or none. For this latter reason, these questions should perhaps be considered as "unanswered" questions rather than as questions at issue. Nevertheless, for important and urgent reasons these questions will be included in this review/analysis with the understanding that the need here is either for answers or for specific recommendations for research that would provide answers. These questions and related explanations/discussion are as follows:

1. What is the maximum range of ozone transport?

The question pertains specifically to ozone, and is concerned with the maximum distance downwind that ozone can travel without excessive destruction or dilution (e.g., no more destruction or dilution than 80 percent). Answers have been offered, but are nonspecific and vary by several tens of kilometers. Thus, from direct observations upon an urban oxidant plume it cannot always be ascertained whether the transported oxidant constitutes a fraction of the concentration at the point of origin or is fresh oxidant formed during transport. Most likely, both types of oxidant exist but in unknown, and not easy to determine, proportions. The question involves considerations of chemistry and meteorology (dispersion) and could perhaps be answered in parts. For example, it would be relevant and useful to answer the following questions:

(a) What is the photochemistry-related lifetime of ozone?

Answers have been calculated for an ideal atmospheric system containing no HC and NO_x pollutants, except for methane (and CO) at their global background levels (5). It is conceivable, however, that in the presence of trace-levels of HC and NO_x — levels such that their potential for O_3 formation is either negligible or predictable — that the lifetime of O_3 may be quite different.

(b) What is the range of ozone lifetimes related to atmospheric (at ground level) on surface destruction processes?

(c) For an inert pollutant, what is the longest lifetime related to the atmospheric dilution process?

2. What is the maximum range of oxidant-precursor transport?

The question pertains to HC and NO_x pollutants as a mixture — not to the individual precursors — and is concerned with the maximum distance downwind that a HC- NO_x mixture can travel without excessive loss of its potential for oxidant formation, (e.g., no more loss of oxidant potential than 80 percent). The question is far more complex than the preceding one on ozone; nevertheless, answers have been offered, although again nonspecific and diverse. For

example, analysis of aerometric data provides evidence suggestive of "long-range" transport but does not identify corresponding source and receptor areas. Also, based on meteorological modeling techniques, it has been calculated that the residence time of air parcels - and their pollutants - in high pressure systems can be as long as several days (6); but this does not necessarily mean that the resident pollutants preserved a significant potential for oxidant formation that long. In general, conclusive evidence is insufficient because the aerometric data available do not distinguish transported precursors from fresh ones, and situations in which precursors travel above entirely source-free areas (e.g., over sea or lakes) are not easy to study. Laboratory and modeling evidence also exists but with the usual uncertainty problems arising from the indirect nature of such evidence. It is the composite of all this evidence that needs to be considered before an answer and/or recommendations can be arrived at.

3. Is it possible to measure reliably the fraction of oxidant caused by local (urban) emissions, and, if so, how?

This question is an extremely important one although it is only a gross simplification of the main question of relating air quality to emissions. To explain, the role of local emissions is in many cases obscured by interferences which, in appearances at least, have extraneous origin. Thus, if the no-interference case is the one in which the local oxidant originates entirely from the day's local emissions, then interferences could be expected to be caused by

- (a) precursors originating from upwind sources,
- (b) oxidant originating from upwind sources,
- (c) precursors originating from local sources but from previous days, and
- (d) oxidant originating from local sources but from previous days.

Of these, only cases (a) and (b) pertain to extraneous influences and, hence, are of interest insofar as this question is concerned, and merit further

examination. Such an examination is made and offered here in the form of a *proposed rather than established picture*; comments, therefore, are solicited.

Precursors from upwind sources may cause an oxidant problem in the source-free rural areas but not in urban areas, since such precursors cannot be expected to be important relative to those emitted within the urban areas; if they are, then the urban area affected should perhaps be redefined to include these upwind sources. For this reason, case (a) can be disregarded as being irrelevant to the question asked here.

Oxidant from upwind sources can affect an urban atmosphere in two conceivable ways: (a) by directly mixing into the urban atmosphere, and (b) by interacting with the photochemistry of local emissions. Obviously, upwind oxidant can be measured directly, and if found absent throughout the day, then it can be concluded that the local problem is caused entirely by local emissions. If upwind oxidant does exist at significant levels, then its main effect is expected to be a direct contribution to oxidant buildup and/or the conversion of an equivalent amount of NO into NO₂. This latter conversion should have an enhancing effect upon oxidant accumulation. The magnitude of these effects must be known if the role and impact of the local emissions is to be correctly assessed.

In conclusion, the question presented here can be reduced or more narrowly defined as follows:

Is it possible to measure reliably the effect of upwind oxidant upon the locally observed peak oxidant, and, if so, how?"

REVIEW AND ANALYSIS

Donald H. Pack

SUMMARY

1. Long distance transport of anthropogenically produced ozone has been convincingly demonstrated to occur over distances up to about 1000 km. Transport over the longest ranges requires a minimized near-surface destruction rate because of either the protective "barrier" of a surface inversion, a slower surface contact destruction rate (e.g., sea surfaces), or the absence of significant concentrations of ozone destroying compounds.

2. Ozone "lifetimes" may be as long as 2-3 days under the above circumstances; the data are insufficient to set a precise upper limit. The "lifetimes" may also be as short as a few hours when the circumstances described above are not evident.

3. There is indirect but rather ample evidence that the highest episodic levels of ozone are related to anticyclonic weather systems moving over significant emission areas. These weather systems maximize solar radiation, and slow ventilation and nocturnal surface radiation inversions. All of these combine to permit an accumulation of ozone and, apparently, ozone precursors. The time scale of these events is on the order of 2-3 days at a fixed point and is directly related to the speed of movement of the anticyclone system. The total effect of the (moving) system may be two to three times as long as it successively affects different areas.

4. There is insufficient data to separate the effects of "fossil" ozone from fresh ozone formed from unreacted ozone precursors on the second and succeed-

ing days of high ozone episodes. Indeed, such precursors are not yet identified, but the scanty evidence favors such a phenomenon.

5. An experimental configuration has been suggested to permit following and measuring a "parcel" of air (the Lagrangian approach) as the most direct and feasible way to determine atmospheric chemistry production and destruction rate and to study the (probably variable) inventories of ozone-related compounds. Such an approach would facilitate understanding the mechanisms of, especially, ozone destruction and vertical mixing by the atmosphere.

INTRODUCTORY COMMENTS

The article by Dimitriadis and Altshuller (1) seems to define the issues as though there is only a single set of physical events: emission-oxidant formation-oxidant destruction unique in space and time. From the data reviewed it appears that while there is a dominant theme, there is enough variation in the physical systems that connect the anthropogenic and natural emissions to the observed oxidant (measured as ozone) levels to raise the possibility of qualitatively different circumstances leading to the creation of high ozone levels. Such items as the variation in the amount and ratios of NMHC and NO_x , atmospheric dilution, "early" vs "late" photochemistry, gas phase and surface contact destruction rates may give rise to quite different end results.

For example, none of the field data were taken in areas where there is the possibility of large natural emissions *only* and the meteorological conditions were optimum for ozone formation. (The negative aspect of the preceding, i.e., "I haven't measured it, but it could exist." is recognized.) However, the experimental data have illuminated the most urgent problem, the urban-to-rural transport/formation of high ozone concentrations. The role of natural emissions was masked by the large anthropogenic emissions. The time seems ripe to perform a similar evaluation over areas with significant natural emissions but (almost) free of anthropogenic sources.

It is important to recognize the possibility that variations in the combinations of the physical mechanisms might, and I emphasize the uncertainty,

lead to different "average" cause-effect relationships geographically and over time.

INFORMATION ASSESSMENT

Question 1: What is the maximum range of ozone transport (dilution and/or destruction equal to or less than 80%)?

None of the data permit a precise evaluation of the question. Elevated levels of ozone, greater than 80 ppb (160 g m^{-3}), created from anthropogenic precursors have been observed after travel distances of at least 700 km (7) and over travel times of 48 hours or more. The anthropogenic character of the source is supported by the concurrent high levels of ozone and CCl_3F , the latter being strictly anthropogenic. This study postulated that the slower contact destruction rate between ozone and the sea surface, together with the minimum dilution characteristic of a large area source permitted long distance transport at sustained high concentrations. It appears that relatively slow vertical dilution and, more importantly, minimum destruction rates were the controlling phenomena. This is supported by the concurrent and contrasting behavior of ozone at land locations where the combination of contact and gas-phase destruction, together with a surface-based inversion that inhibited replenishment of ozone from sources aloft, reduced surface level concentrations from more than 100 ppb to less than 50 ppb in a few hours.

A study of the dilution of CCl_3F and CCl_4 moving from Europe to Ireland (8) suggests that a travel time of about 120 hours without additional emissions into the volume is sufficient to dilute inert pollutants from a large area source to values near background levels.

None of the field data come close to the continuous surveillance of a moving parcel of ozone and precursor-rich air over sufficiently large time-space coordinates and free of additional emissions. Such data are required to provide accurate answers to the question.

References presenting field data are consistent in showing that area-wide, nonurban, high ozone episodes require significant anthropogenic emissions, some level of UV radiation flux (never specified), and not too vigorous atmospheric dilution. References 6, 9-15 emphasize the large area episodic situation characterized by anticyclones moving, not too rapidly, across multiple emission sources and the cumulative buildup of high ozone concentrations as new emissions add to "fossil" ozone (either ozone *per se* or from late reacting precursors).

The ozone "lifetime" at a point then becomes much more the speed of motion of the synoptic systems. Climatological studies indicate that these situations tend to be more prevalent in the eastern U.S. and more likely in the fall and early winter, not in summer at the time of the maximum solar radiation. These studies also show that "episodes" of 2-days' duration at a particular location should be fairly common, but that duration of an episode, at a point, decreases markedly to about one per year north of 35° N Lat. and near two per year in the southeastern states.

No data were available for this area of the country, which appears to be particularly vulnerable to the episode phenomenon providing the emissions are sufficiently large.

It seems clear from the data presented that: (a) large area buildups in high ozone concentrations involve air parcel residence times of at least 2 days to accumulate sufficient source material (6); (b) "fossil" ozone carried aloft by daytime convection (but not too far aloft) must be prevented from mixing downwards to the surface at night, usually by a surface-based inversion, to reduce the near-surface destruction if it is to survive in sufficient quantity to influence the following day's ozone concentration. This is shown most clearly by the "DaVinci" data (16).

In contrast several papers (16-27) demonstrate directly augmented ozone levels resulting from transport over 6-8 hours and distances from 100 to 300 kilometers. In these instances ozone concentrations continue to increase with

time and distance from the primary source area (e.g., New York to Boston). It appears (19,22,28) that this condition is due to not only delayed ozone formation downwind from the primary source but also to the fact that the production rate exceeds the combined gas-phase/contact destruction rates even though vertical mixing remains moderately active.

With this preamble one can estimate answers to:

What is the photochemistry-related lifetime of ozone?

Under circumstances of minimal surface contact destruction and a major reduction in the concentration of compounds that cause gas-phase destruction (e.g., NO), the demonstrated lifetime is at least 48 hours. This has been shown to occur for transport over the sea and (for somewhat shorter times) over land at altitudes above 100 to 300 meters in the presence of a surface inversion.

Under circumstances permitting contact destruction and continued emission of gas phase destruction compounds, the lifetime is less than 6 hours, probably nearer to 2 hours. For example there are a few data that can be used to make crude estimates of this latter effect. The following ozone concentration data were extracted from Figure 6 in Decker et al. (16).

TABLE 1. OZONE CONCENTRATION ($\mu\text{g m}^{-3}$)

	Maximum	Minimum
Surface	285 (1800LST)	59 (2300LST)
Aloft(800m)	291 (1830LST)	236 (2315LST)

The reduction in ozone aloft can be postulated to be due to only O_3 -NO gas-phase destruction. The reduction in the ozone concentration, $55 \mu\text{g m}^{-3}$, occurs in 4.75 hours. If we assume that this decrease in ozone also represents the rate of reduction in NO, and if we further assume an exponential form for the decrease, this results in an NO "half-life" of 0.82 hour. Assumption of a linear decrease gives the obvious value of $12 \mu\text{g m}^{-3}$ per hour.

If these values are applied to the surface data that show a decrease of ozone of $226 \mu\text{g m}^{-3}$ in 5.0 hours, the exponential NO decay model would account for almost 99% of the reduction, leaving very little to surface contact removal. (The linear removal rate would account for only $58 \mu\text{g m}^{-3}$ with the remainder to be destroyed by surface contact. However, since this requires the exhaustion of all the NO as soon as the $58 \mu\text{g m}^{-3}$ of ozone is destroyed with no replenishment of NO, this seems an illogical model.)

The actual reduction of surface ozone, 285 to $59 \mu\text{g m}^{-3}$, if the reduction rate is of exponential form, suggests a half-life of somewhat more than 2 hours.

This arithmetical exercise suggests that the gas-phase, removal mechanism reduces ozone by 50% each 1 to 2 hours with the surface contact removal rates over land somewhat slower, on the order of 2-4 hours when couched as a "half-life." However, the crude assumptions and lack of data suggest treating these numbers with considerable caution!

What is the range of ozone lifetimes related to atmospheric (at ground level) on-surface destruction processes?

One attempt to estimate such numbers has been given above. However, this issue cannot yet be satisfactorily disentangled from the gas-phase destruction. Flux measurements (e.g., 1×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$) can be questioned unless ancillary measurements of possible ozone-destroying compounds are also reported. Estimates of global residence times refer to the total troposphere, not to the contact layer. These estimates of about 4 months (29) are much too long for this smaller volume.

Assumption of a deposition velocity approach using v_g values similar to other reactive gases (e.g., iodine- $v_g = 2.5 \text{ cm s}^{-1}$; SO_2 - $v_g = 0.85 \text{ cm s}^{-1}$) would deplete the contact surface layer of ozone in a few minutes, unless replaced by transport from above. This may be too rapid a removal rate for a layer of finite depth of, say, 10 to 100 meters. Here the rate-limiting

process is not the actual destruction but the downward turbulent flux of ozone. At night this may be slower than the "deposition."

Thus with the data now at hand we must again resort to pure empiricism and guess at values. Considering a surface layer of 10-100 meters thick, values seem to range from near 2 hours overland to a few days for overwater trajectories.

For an inert pollutant, what is the longest lifetime related to the atmospheric dilution process?

The question as stated, even for "no more destruction or dilution than 80%," is not meaningful unless one specifies the source configuration, size, location, and intensity of emissions. To take an extreme example, natural particulates with their hemispheric-wide source distribution are estimated to have a lifetime of about 30 days. Anthropogenic halocarbons may reach levels of near 1000 ppt(v) on the outskirts of cities, but the global background is still near 15% of these values even after circling the globe.

In contrast, a single point source, even in modest dilution conditions, is reduced by about 10^{-4} within a kilometer of travel.

On a more relevant air pollution scale, if the source region is of sufficient lateral extent, say 2000 x 2000 kilometers, atmospheric dilution is primarily confined to the vertical dimension, with this determined by the day-to-day variation in the maximum mixing depth (MD). Day-to-day changes in the MD are usually rather small, especially in the anticyclone conditions so frequently responsible for area-wide high ozone episodes. Examination of the combined MD/wind speed data of Holzworth (30) show day-to-day variations in the afternoon MD of 10-20% together with light and chaotic wind conditions. The day-to-night variation is much larger. Typical values for summer would be about 1800 meters in the afternoon and near 400 meters at night, or rather the following early morning. Wind speeds averaged over the afternoon depth are about 5 meters per second and 3-4 meters per second over the morning MD.

A crude model of dilution can be constructed from these data. Assume a uniform distribution of an inert material throughout the 1800 MD. With the onset of stability the upper 1400 meters (1800 - 400) are isolated from surface sources and carried away at the difference in wind speeds between the two layers, 2 meters per second. However, double this to 4 meters per second to account for the higher winds aloft at night. In 12 hours this volume moves about 170 kilometers. Then let the MD of the next day increase to 2700 meters (a very large change). This reduces the concentration in this isolated volume to about 50% of its original value. Wind direction shear with height would result in some additional dilution but probably less than an additional factor of two.

Under such conditions and for large area sources, the reduction in concentration due to atmospheric dilution alone is unlikely to be more than 75% in a 24-hour period, probably less.

An alternate approach is suggested by Decker et al. (9) with the concept of "residence time" within an anticyclone. These calculations suggest a residence time of 1-3 days within the system. Again vertical mixing is the primary atmospheric dilution mechanism. Since these systems do not show large variations in vertical mixing, dilution on the order of 50% per day is reasonable leading to periods of 2-3 days required to reduce concentrations to about 20% of the original value.

Note that both of these crude estimates are compatible with the interesting trajectory/statistical analysis of Ludwig et al. (31). The space scales for high ozone episodes were near 450 kilometers for 12 hours and 1150 kilometers for 36 hours in this study.

Finally a few measurements of the near inert gases, acetylene and propane (9), indicate little or no dilution across a distance of more than 1600 kilometers (Des Moines, Iowa - Albany, New York). Since emissions are added from below, these data cannot be used to directly calculate dilution, but the lack of variation of more than a few tenths of a percent confirms the absence of rapid dilution between significant source inputs.

Question 2: What is the maximum range of oxidant-precursor transport?

I was unable to locate any quantitative information from which direct answers to this question could be derived. The weight of suggestive evidence is that the more highly reactive precursors are "used up" in the first day's photochemistry and that "maximum" range must be defined in terms of "highly," "intermediately," and "slowly" reacting classes of materials. Ludwig et al. show a correlation between high ozone levels and NO_x emissions 24-36 hours earlier (31). This in turn relates to distances of transport of 700 and 1150 kilometers. The difficulty with this information is that it cannot separate the contribution of "fossil" ozone from any fresh ozone created from previously unused precursors. (See Ref. 18, for example.)

The mathematical models presented seem equivocal and too simplified to presently contribute much to the quantitative answers.

However, the chamber experiments of RTI (32) indicate a capability for ozone formation is retained for 2-3 days without additions of more source compounds. If true for the outdoor atmosphere, this translates into distances of 1000 kilometers or more.

Question 3 and the final, unnumbered question are also related to Question 2.

Question 3: Is it possible to measure reliably the fraction of oxidant caused by local (urban) emissions, and, if so, how?

Is it possible to measure reliably the effect of upwind oxidant upon the locally observed peak oxidant, and, if so, how?

All of these questions involve solutions to a multidimensional problem that involves at least the following:

Emissions - O_x , NMHC, NO_x
UV Activation energy levels
 O_x - Formation/destruction mechanisms and rates
 NO_x - Formation/destruction rates
NMHC - Changes in composition by "classes"
Atmospheric transport
Atmospheric dilution in x, y, z space
Time

Since the data now at hand do not appear to be adequate to resolve these issues, I believe that the most promising approach is to design field studies to consider the preceding parameters in a Lagrangian framework with Eulerian supporting data. The DaVinci experiment suggests that this would be a very profitable approach.

Concurrently mathematical photochemistry models tailored to Lagrangian type of data should be prepared. The models can also assist in the design of the necessary measurements, both the compounds ("classes?") and the observational frequency requirements. I am not qualified to comment on model design.

Also, I cannot comment on the reliability aspects of the experimental configuration to be suggested since this aspect seems, to me at least, to depend mainly on air quality instrumentation - its sensitivity, precision, accuracy, and the capability of rapid repetition rates, at least for most of the compounds.

Assuming, however, that the requisite instrumentation can be assembled, the following experimental configuration is suggested.

Lagrangian Photochemistry Experiment

Platforms:

- Free floating balloon(s): Equipped to measure O_3 , THC, NMHC (by

"classes?"), NO, NO₂, CCl₃F, nephelometer UV radiation intensity, temperature, relative humidity, and height (pressure).

- Surface platform(s), car or boat: Equipped as above.
- Aircraft: Equipped to measure O₃, NO, NO₂, THC, CCl₃F, nephelometer, temperature, relative humidity, and height.
- Upper wind systems
- Temperature profile systems
- Small constant volume balloons (tetroons): radar and/or visual tracking.

The free balloon would measure *in situ* time changes. Comparison of its data with the data from the surface platform and aircraft air quality profiles would permit estimates of vertical fluxes and of destruction rates. Horizontal traverses by the aircraft would provide data on x-y gradients (inhomogeneities). Vertical wind and temperature profile data are essential, especially the latter, to study the rarely measured time-change in the mixing depth and the upward extent of the near-surface nighttime stable layer.

The crucial aspect of this experiment is the selection of the experimental site(s). An essential experiment is the tracking of an urban emission volume (e.g., the emissions from 0800-0900) for 24 to 36 hours to study ozone and precursor behavior and interaction, to measure quantitatively the "fossil" vs "fresh" ozone. It is necessary to have complete assurance that there are zero emissions along the track of the free balloon to eliminate the problems posed by the present mixed data.

One possibility is to launch in the plume from a relatively isolated coastal city (Charleston, S.C.?) with a trajectory moving offshore 10-20 miles then, hopefully, paralleling the coast but entirely over water. The feasibility of this from the standpoint of the safety of the balloon crew may be

marginal at best. The possibility of automated instrumentation on a radio-controlled, unmanned large balloon should be investigated.

A second possibility is a site near Lake Michigan or Lake Superior; Chicago, Milwaukee, or Duluth might serve as the city source.

A third possibility is to stage the experiment in the land-sea breeze regime of the Los Angeles Basin through the use of the offshore islands as launch points. The stringent air traffic controls and crew safety may create difficulties.

Lastly, and less desirable, would be the selection of an isolated smaller city (Spokane, Washington, Portland, Maine?) where the "no additional emission" criterion might be approached.

(Note: Portland, Maine, was suggested, which raises the issue of the role of natural emissions. While the data available do not seem to show any large natural influences, one can also infer that in the areas where the data were collected and at the times of the experiments the anthropogenic emissions were too overwhelming to permit detection of the effect of natural emissions. It seems desirable to collect some preliminary data to evaluate the need for a "DaVinci" type of experiment over, for example, rural North and South Carolina during slow dilution, high radiation intensity conditions.)

Use of the Lagrangian approach for data to answer the final (unnumbered) question may not be practical for air traffic and safety reasons since it would involve deliberate free ballooning over a city. However, it should be possible to use this approach to measure the pollutant from upwind to the edge of the city, then shift to a helicopter platform following a tetroon over the city. This technique was used very successfully in the LARRP. Support of a ground air quality network would be essential. St. Louis, Missouri, seems a logical site choice.

REVIEW AND ANALYSIS

Elmer Robinson

INTRODUCTION

One of the very urgent problems in the Federal Government's drive to achieve cleaner air is to obtain some degree of improvement in the area of photochemical air pollution. This initially meant bringing oxidant and ozone concentrations observed in urban areas down so that the prescribed ambient air quality standards were met in the nation's urban areas. This ozone/oxidant program has been proceeding slowly through an urban source control program directed at the control of the oxidant precursors of nitrogen oxides and reactive hydrocarbons. Transportation sources were major contributors in these areas and were the target for a variety of control plans and actions. The control program for obtaining control over photochemical oxidant* was directed at sources in the general vicinity of the observed excessive concentrations or over surrounding regions having an obvious strong impact on the area where the excessive O_3 levels were measured. Thus this was a "local source-local control" program, and the various EPA regulations were established on the premise that excessive O_3 would be countered by a program of source control in the general area of the excessive O_3 observations.

This program of local source-local control began to come under attack when excessive ozone concentrations were measured in rural areas where there were few obvious local sources. One of the first of these ozone-affected rural areas was in the mountains of western Maryland. Even if very restrictive local source control options were followed in these local areas, it was obvious that the O_3 levels would persist unaffected. This would occur because

*Ozone or O_3 will be used in the rest of this text to indicate photochemical oxidant.

it was recognized that large-scale atmospheric transport of O_3 was capable, in certain situations, of advecting air with high concentrations of urban pollutants, O_3 , and ozone-precursors into the remote areas. If ozone advection was a general rather than just a peculiar condition, then some revision in the source control strategies directed toward photochemical oxidant would be called for. At the time this report is being prepared (early 1977), there are still many confusing aspects present in the urban-rural photochemical oxidant situation. This report is directed toward an examination of various meteorological transport features and problems that are associated with photochemical oxidant in rural areas.

Some of these O_3 transport problem areas have been outlined by Dimitriades and Altshuller (1) to include the following areas:

- The importance of natural versus anthropogenic O_3 in rural areas;
- The possibility that O_3 transported from upwind sources could obscure local problems, e.g., the areas where emission controls should be established or perhaps the local relationship between O_3 and precursors;
- What is the maximum range of significant O_3 transport?
- What is the maximum range of significant O_3 precursor transport?
- Can sources for both advected and local O_3 be quantified when O_3 is advected into an area?
- What control strategies can be proposed that will account for some expectation of success in lowering observed O_3 levels?

The following discussion will consider these various problems from the basis of a critical examination of the available current literature.

NATURAL VERSUS ANTHROPOGENIC OZONE

Introduction

Ozone is a natural constituent of the atmosphere and has been reported by various authors as having a ground surface concentration up to about 50

ppb (33). The source of this natural ozone has typically been attributed to the injection of ozone into the troposphere from source regions in the stratosphere. There is no doubt that ozone of stratospheric origin exists at the surface and that this is a major source for the ozone found in many remote areas.*

The current literature on rural O_3 and O_3 transport shows both similarities and differences in various regions of the country. Thus there may not be a single model or explanation that can be fitted to all regions of the country or, indeed, to a single region for all types of seasonal episodes or circumstances. The discussion below will consider three major areas of the U.S. where the rural O_3 problem seems to pose regulatory problems at the present time. These are the gulf coast, the upper Midwest, and the Northeast. California problems will not be considered in detail because no nonanthropogenic explanation of the O_3 patterns in this area makes any sense. The California situations can, however, provide data on and some support to models explaining O_3 conditions in other regions.

It should be recognized that what were probably the first situations where natural ozone was suspected as being a significant air pollution factor occurred in southern California. The first was the initial characterization of the oxidant in the Los Angeles photochemical smog as being caused by local, urban precursor sources. A second event that is not recalled often is the explanation of the high oxidant concentrations, over 300 ppb oxidant in some cases, accompanying the "clean" onshore sea breeze in rural northern San Diego County in the later 1950's. The cause of these very high, by Midwest and east coast standards even now, oxidant levels was described by Bell who showed that overwater trajectories of smog from the Los Angeles basin could be identified with the high oxidant incidents in San Diego County (34). In these meteorological

*This author would like to define the two terms "remote" and "rural" to have the following specific meaning: "remote" is defined as being removed from any possible identifiable anthropogenic source, e.g., an Arctic tundra station; "rural" is a nonurban location that from time to time may be influenced by man's activities at an identifiable source area, although the mechanism by which the pollutants affect the given location may not be readily recognized, e.g., an upstate New York station.

logical situations, characterized by offshore flow in the Los Angeles area and onshore winds in the San Diego area, the ozone and/or its precursors persisted overnight and into the next day. In addition the pollutants traveled about 100 miles until the smog parcels were observed as high oxidant incidents in an area of minor emission rates. Before Bell made his careful study, it might have been concluded that this was natural ozone because it was carried by a sea breeze coming off a source-free area.

Most investigators in this area of natural versus anthropogenic ozone in rural (not remote) areas believe that their results indicate anthropogenic influences as being the cause of O_3 levels above the 80 ppb National Ambient Air Quality Standard (NAAQS). The study by Decker et al. at Research Triangle Institute (RTI) is one of the more definitive research programs in this regard (16). Two large geographic areas were covered by RTI in extensive aerial and ground monitoring programs.

Gulf Coast and Texas Areas

One of the RTI study areas included the Texas-Louisiana gulf coast and extended over both land and water areas in the summer and fall of 1975. This gulf coast study area is of particular importance because earlier assessments of Texas O_3 levels had led authors to conclude that widespread O_3 concentrations could not be explained by anthropogenic factors because O_3 was frequently high with onshore winds at stations such as Corpus Christi. Thus it was concluded from these early local studies that the O_3 must represent the impact of natural sources.

In a subsequent assessment of the "Texas problem," Price came to the conclusion that high O_3 days in Texas (days having a maximum 1-hour average O_3 greater than 150 ppb) were normally the result of the combined effects of old photochemical pollutants and fresh new pollutants (35). The accumulation of sufficient ambient concentrations was favored by weak winds corresponding to weak pressure gradients associated with the synoptic weather accompanying the high O_3 periods. Price concluded that local sources were the major problem in Texas although some transport over larger areas could have been involved.

Price determined that correlations of maximum O_3 levels with other cumulative pollutants or pollutant effects such as CO , nonmethane hydrocarbons, NO_2 , or visibility were not significant or especially informative. This result is in contrast to the higher and apparently significant O_3 general pollutant correlations reported by Husar et al. (13) and may be indicative of geographic differences in this large scale or "air mass" O_3 problem.

The conclusion that natural tropospheric O_3 was not a factor in the high O_3 events in Texas was also supported by Price's review of the prevailing synoptic weather systems. It was shown that none of the high O_3 days was associated with frontal passages which would be generally indicative of wide-area vertical motion and deep tropospheric mixing.

In contrast to the study of Price, which was based on a careful assessment of available data from a number of sources, the RTI gulf coast study (16) was a comprehensive ground and aerial sampling research program that included, in addition to O_3 measurements, supporting data on nitrogen oxides and hydrocarbons. Both aircraft profiles and ozonesonde measurements were made to provide O_3 data on the upper layers of the atmosphere.

The analysis of the RTI aircraft data showed that there were four identifiable aerial distributions of O_3 in summer and fall seasons in the gulf coast area:

- Area-wide low concentrations, i.e., O_3 up to 35 or 50 ppb.
- Localized plumes downwind of major source areas.
- General, larger than a plume, regions of elevated O_3 where some values exceeded 80 ppb, and where the concentrations in various situations tended to increase from west to east.
- Large area (e.g., Louisiana to North Carolina) O_3 concentrations generally exceeding 80 ppb.

Some of the more important facts about the gulf coast O_3 situation were concerned with the meteorology of the high (and low) O_3 events.

As Price had noted, the RTI study found that slow moving air (i.e., weather systems with weak winds and weak pressure gradient) moving over large hydrocarbon sources was associated with the higher concentration O_3 events at both urban and rural locations. The wind trajectories associated with these high concentration situations characteristically show anticyclonic curvature indicative of flow in a high pressure system. By way of contrast, situations with stronger winds and less of a tendency for anticyclonic curvature showed lower O_3 levels. Trajectories with long overwater fetches were also associated with lower O_3 concentrations. In those situations when elevated O_3 was measured over the Gulf, trajectory analyses usually were able to show that the air stream had a relatively recent (within 24 hours) history showing passage over land areas and often over concentrated source areas. The documentation of this type of an event is obviously the answer to the much earlier Texas examples of high O_3 in the onshore sea breeze at places like Corpus Christi. The finding is obviously similar to Bell's California result.

Trajectories in the Texas area also documented situations of inter-city transport, and one such situation may have been the cause of O_3 in excess of 80 ppb at Austin (16).

When area-wide high concentrations were observed, a stable layer that could limit vertical mixing was usually observed below 2 km. This would also be characteristic of a large, high pressure system. The observation would also be consistent with the data from the ozonesonde observations showing that although mid- to upper-level ozone concentrations could change by 50% during a day, these changes did not reach to the lower layers of the atmosphere and affect ground-level O_3 concentrations.

Thus the conclusion reached by both RTI and by Price that anthropogenic emissions are the main cause for O_3 values exceeding 80 ppb in the Texas gulf coast seems well founded.

Upper Midwest Regions

In the area of the upper Midwest there are two groups that have carried

out extensive O_3 studies that are relative to both O_3 transport and to urban/rural relationships. The two main groups that will be cited in this analysis are RTI (16) and the Washington University group (13,36).

In these major studies in the upper Midwest, the RTI program attempted to follow developing high pressure systems as they moved eastward from Montana (16). Tracking was done by aircraft, a string of ozone monitors on the ground, and an ozonesonde program. The program of Washington University was directed toward assessments of the urban plume from St. Louis that typically stretched to the northeast of the city (13). This group also analyzed some air mass transport systems on the basis of areas and periods characterized by low, non-fog visibility.

The RTI upper Midwest study showed that high O_3 concentrations in the summer months across these states were associated with the passage of high pressure systems. Within the anticyclone, the lowest O_3 concentrations are found in the leading or eastern portion of the anticyclone, and the highest concentrations are found in the trailing or western portion of the cell. This pattern has been recognized for a number of years and has been described by different authors on the basis of independent investigations (31,37). The change in O_3 in the anticyclone is attributed to the fact that the air parcels in the leading portion of the system have had the shortest residence time in the anticyclonic regime and thus the least exposure to anthropogenic pollutant sources under synoptic conditions favorable for pollutant accumulation. This is in contrast to the fact that in the trailing or western portion of the high pressure area the parcels would in general have accumulated the largest exposure time to anthropogenic sources and to weather conditions favoring pollutant accumulation. In terms of travel across the multistate area the daily maximum concentration or the total hours exceeding 80 ppb O_3 increased in the high pressure system as it moved from west to east.

In North Dakota, near the origin region for the systems followed in this migratory anticyclone study, a series of ozonesonde flights in 1975 failed to show that O_3 intrusions from the stratosphere were important in the surface layer chemistry. Thus it was concluded that natural O_3 was not an important

factor in the subsequent development of excessive ozone in these moving weather systems.

These moving, high pressure areas gradually accumulated concentrations of other pollutants as well as O_3 as the system moved along. This was shown by hydrocarbon and halocarbon measurements as well as by the sulfate and nitrate content of the total suspended particles in the atmospheric samples.

Comparative analyses of changes in the average weather patterns for 1973, 1974, and 1975 were made. It was determined that, of these several years, 1975 had fewer hours of high pressure, less high O_3 , and lower average O_3 during the passage of high pressure systems. This phase of the study points out clearly that year-to-year changes do occur, and thus such facts must be accounted for in programs dealing with photochemical oxidant.

The vertical motions that are usually postulated for a high pressure system do not explain the higher O_3 levels on the back side of the system. Subsidence and surface divergence are usually most pronounced in the center and in the leading edge of the high. This should be accentuated by the vertical motions related to the preceding trough and frontal system as well. The RTI report thus argues that the increase at the surface was due to an increase in O_3 synthesis in the surface layers. Likewise, it is concluded that there is an increase in O_3 synthesis in the eastern areas of the U.S. as compared to regions in the west.

The RTI authors made some detailed model calculations to estimate the likely residence time within a high pressure system of air parcels having an origin in various parts of the system (16). It was determined that parcels initially in the northeast quadrant had the longest potential resident time, about 6 days, and that parcels on the western side of the circulation pattern had been in the system the longest time. This latter conclusion is in general agreement with O_3 measurements in pollutant source areas such as have been described by Westberg et al. (37). A very important point is made by the RTI authors (p. 161): an air parcel does not move across the country as a permanent part of a high pressure system. Rather, it is a case of a parcel moving

in on one side of the system and out on the other as the pressure pattern moves across the area. Only under a weather pattern with a unique series of coordinated systems would there be a direct net transport of air from area to area continually under the influence of a given high pressure system. With this in mind, the RTI findings that O_3 patterns in the west and the east must be explained by different chemical relationships between precursors and destructive agents points up the rather obvious fact that emission characteristics are different in the two areas. The fact that both areas observe higher concentrations of O_3 with the transit of a high pressure system is probably an example of concentration effects rather than a result of similar chemistry.

With regard to transport, the set of model calculations by RTI would appear to show that even though the continuous travel of air pollution effects (e.g., lowered visibility) can be mapped across the country, perhaps for 200 km, the individual air parcels and their entrained pollutants had much shorter residence times within the anticyclonic weather system. The haze "blobs" studied by Husar et al. (13) are a case in point. In this case hazy conditions as a result of entrained air pollutants were tracked from June 25 until July 5, 1975, a period of 10 days. The "blob" of low visibility conditions was initially observed in the Midwest near St. Louis on June 25, and after a tortuous path, was determined to be affecting Atlanta, Georgia, on July 5. As indicated by the RTI model, single parcels and given masses of pollutant would not persist in the system for such an extended period. What does persist, however, are the atmospheric conditions that favor the accumulation for periods of one to a few days of pollutants from a succession of more local sources at relatively high concentrations. Since some considerable amount of wind movement is necessary to produce a long-distance transport system and at the same time low winds are necessary to produce a high concentration of pollutants, there must be some sort of delicate balance among the factors of source strength, dilution by wind, and transport flow.

The studies in the St. Louis area have included a large number of groups and these have produced an even larger number of papers, many of which have dealt with O_3 transport from the St. Louis urban area (13,36,38). These

papers as well as many others show a reasonably consistent picture: an urban plume is found stretching downwind, typically toward the northeast, from St. Louis for distances of up to 160 km (36). At times White et al. report O_3 concentrations occurring in excess of 300 ppb. Weather conditions obviously have to be favorable for long distance transport and minimum dilution during such travel. These are typically found in the anticyclonic systems that traverse the area in the summer. This results in a situation where the urban plume is imbedded in an already dirty air mass. For example, White et al. note that on July 18, 1975, when the St. Louis urban plume was detected by aircraft sampling out to 160 km, the air mass O_3 concentrations outside the plume were at levels up to 70 ppb at the 160 km distance. Thus the whole air mass affecting the region was accumulating a significant background of O_3 even while the major urban plumes were making significant contributions. The fact that the St. Louis plume was so persistent under conditions when the whole air mass had above normal concentrations of ozone is considered by this author to be due to meteorological factors being present in the high pressure area and not to a chemical synergistic system between the air mass and the urban plume.

The intensity of the analysis of the St. Louis Plume has led to attempts at chemical modeling of O_3 reactions in the plume system. White et al. conclude that the apparent O_3 yield on the basis of hydrocarbon emission rates is close to the stoichiometric upper limit (36). Some arguments are made that this apparent high yield may be due to the influences of unaccounted-for hydrocarbons brought into the area as part of background concentrations, as mentioned above. No data are brought in to support this argument. However, the air masses where such enhanced O_3 formation apparently occurs has supported considerable O_3 formation already, as indicated by the observed 70 ppb "background," the St. Louis plume may be gaining some additional O_3 from a revitalization of spent urban emissions present in the air mass as it moves across St. Louis. This level of anthropogenic emissions should not be confused with natural or biogenic emissions.

In transport situations it is important to differentiate between a biogenic emissions background and an anthropogenic background. The biogenic air mass background, such as was observed by RTI in Montana anticyclones, has been

shown by Grimsrud and Rasmussen to be poor in NO_x and to have a strong ozone-formation potential after the addition of NO_x (39). In contrast, an anthropogenic air mass background as is characteristic of rural areas in the Midwest shows little O_3 response to an increase in NO_x . In fact in many cases the response of experimental air parcels is a decrease in O_3 formation compared to an air parcel that contains only the ambient air NO_x concentration. This has also been shown by Grimsrud and Rasmussen.

Thus across the northern part of the U.S., from Montana to the east coast, there is strong evidence for the existence of a west to east gradient of photochemical O_3 production. Because single air parcels do not complete this total track, the buildup and change in the O_3 content of anticyclones should be attributed to changing characteristics of regional sources, especially in the density of sources, and perhaps to an increasing intensity of the moving anticyclonic systems. In the Midwest and probably on the east coast, air mass background levels are more characteristic of a spent urban pollutant mixture and may show a negative potential for producing O_3 with an increase of NO_x . Thus when an urban plume is dispersed into a Midwest high pressure system, it must possess all of the O_3 precursors and not just the NO_x levels as might be the case for a clean biogenic background. Because of the higher levels of pollutants in an anthropogenic background situation, and the likely presence of O_3 scavengers, the impact of an urban plume would probably be less than would occur in a cleaner biogenic background. Along the gulf coast it has already been mentioned that urban plumes marked with excessive ozone were readily detected. This may be indicative of a lower anthropogenic background in this region. However, the background measurements of RTI always showed some levels of anthropogenic emissions, so the gulf coast was not an example of a biogenic background area (16).

Northeast U.S. Regions

The northeastern part of the U.S., including the area generally north and east of Philadelphia, contains a dense population and probably has the largest, most congested, commercial-industrial area in the U.S. in the area of New York and New Jersey surrounding New York City. In addition, the long coast line

complicates the regional wind patterns by introducing local land and sea breeze effects.

Oxidant patterns over the Northeast have received considerable attention because high concentrations have been measured almost routinely in rural and distant suburban areas for a number of years. One group that has led in the regional analysis of this area has been the Bell Laboratory group under the leadership of W.S. Cleveland and T. Graedel. Their work has emphasized the interpretation of the air quality data, particularly ozone, by the various agencies in the area rather than in mounting a field measurement program.

The result of the Bell Laboratory work has been to show clearly the urban plume effects in this area and the displacement of maximum O_3 concentrations downwind of major source areas such as New York City and Philadelphia. The regional transport in this area that is most important for O_3 control strategy is the travel to the northeast of the New York City - New Jersey urban plume with apparent effects in Connecticut and Massachusetts (40). This transport is characterized by a number of features that are not unexpected, given our present understanding of the urban photochemical reaction system. These are:

- The central urban areas show low O_3 levels because the transport of effluents out of the city moderates the pollutant concentrations, the time required to form O_3 levels, and the high concentrations of NO_x scavengers in the local emissions.
- The highest O_3 concentrations occur outside the main urban area along the wind trajectory at a distance determined by 1-2 hours of midday wind travel.
- These peak O_3 concentrations occur during the early afternoon at the time of maximum solar radiation.
- Beyond the area of peak O_3 concentrations the average time of the peak O_3 is progressively later in the day and is considered indicative of the movement with the regional wind of the peak O_3 formed earlier in the day.

- Although there are undoubtedly O_3 impacts from the larger local urban areas along the track of the New York City plume, these are frequently overshadowed by the transport from the New York City source area.

These previous statements are based generally on the statistical analysis by the Bell Laboratories group of summer season O_3 data files (40).

The assessment of individual days and O_3 events in the Northeast has been carried out by a number of groups including Washington State University (37), Battelle-Columbus (41), and EPA-Las Vegas (28). These analyses resulted from the extensive 1975 Northeast Oxidant Survey involving these three research groups. In general the results are in agreement with the results from the Bell Laboratory research and the importance of O_3 advection across the area has been clearly established. One feature that the daily research data show clearly is the importance of the urban plume from New York City moving eastward along the southern shore of Long Island. This situation is not well defined by the Bell Laboratory results. This plume south of Long Island forms a source for O_3 concentrations occurring along the Connecticut and Rhode Island coasts under typical sea breeze patterns. These coastal areas can receive significant advection of O_3 from the New York City urban plume under wind conditions that do not carry the plume directly over land areas (37).

Spicer was able to develop a simple regression expression to relate ambient O_3 and fluorocarbon levels at two rural Connecticut locations. Since the fluorocarbons are unique, stable anthropogenic emissions, these regressions provide strong evidence for the impact of the urban plume at Simsbury and Groton, Connecticut. These results obviously would apply to other areas as well.

Weather patterns seem to play a lesser role in establishing O_3 pollutant levels in the Northeast than is seen either in the Midwest or gulf coast areas. It is, of course, recognized that the general pollutant loads reflect the general weather patterns, but it seems that, on a subjective basis, there is a much broader set of weather conditions that can accompany the occurrences of high O_3 levels in this area and less sensitivity, for example, to the

location or intensity of an anticyclonic system. This could be a result of the population density over the area and the relative dominance of urban plumes over the anthropogenic background levels in the air mass.

Local circulations in the surface layers play a dominant role along the coastal areas in the Northeast as noted by Westberg (37). This dominance was not as apparent in the Midwest and gulf coast areas, although important local systems have been noted in the Great Lakes area particularly around Chicago.

Discussion of Transport Relative to Natural Ozone Sources

In general, this writer is of the opinion that the dominant effect represented by rural O_3 concentrations is the transport of anthropogenic pollutants. It is recognized, however, that there are areas where natural O_3 and, in particular, stratospheric O_3 may occur in important concentrations. As previously mentioned in the gulf coast discussion, stratospheric intrusions of O_3 are related to strong cyclonic storms that affect a deep layer and result in a breach of the tropopause at the polar jet stream. Danielsen and Mohnen have assessed tropopause folding as one specific mechanism for the injection of stratospheric ozone into the troposphere (42).

The question of the importance of natural O_3 , in what would probably be described as an anthropogenic background situation, comes up in the several papers reporting measurements on Whiteface Mountain, New York, by Mohnen and Coffey and their associates (42-44). In these papers the fact that O_3 concentrations measured at the top of Whiteface Mountain (altitude 4860 ft) show patterns that are out of phase with urban and rural stations at lower altitudes is used to support the importance of a stratospheric O_3 source in up-state New York. The analysis is not convincing in that when downward transport of O_3 is argued the pattern could also be explained by a transport of destructive or scavenging factors out of the nearby urban areas and a longer residence time of photochemical O_3 at the elevation of the mountain top under less pressure from scavenging reactions. The increased persistence of O_3 in upper layers of the atmosphere has been documented in detail in southern California. This would seem to be a better explanation of the Whiteface observations than is stratospheric subsidence, except when situations of

tropospheric folding are likely in the vicinity. These would be mostly present in the spring. There is no reason that a single cause has to be given for all situations at this location.

Ozone reported at the ground in remote locations may well be due to stratospheric injection (45) or to photochemical reactions involving natural hydrocarbons (46). Chatfield and Harrison show that O_3 measurements in a remote coastal area of the Pacific Northwest may range up to about 70 ppb with the mode for monthly data between 40 and 55 ppb. When high natural ozone occurs there are generally indications of more vigorous weather systems, and under such conditions there seems to be little chance for confusion with the summertime anticyclonic type of high ozone incident. The question of natural biogenic hydrocarbon production of O_3 is harder to resolve and separate from the anthropogenic system because the photochemical production would be a maximum under the same conditions that the anthropogenic cycle would. However, the biogenic concentrations would be lower, and at present there seems to be no evidence of excessive (i.e., concentration of 80 ppb or higher) O_3 production from just biogenic emissions.

TRANSPORT FROM UPWIND SOURCES AND LOCAL PROBLEMS

Ozone transport from one urban area into a less dense or smaller urban area can be a major factor in the O_3 pattern observed in the smaller area. Such situations are observed clearly in the Northeast because of the massive nature of the New York City urban plume. Along the coast of Connecticut, it is usually immaterial whether the emissions from small towns such as Groton are included in the daily O_3 pattern or not since the O_3 concentrations are dominated by the New York City urban plume carried by the sea breeze. The obvious question in the Northeast is how big does the downwind city have to be before less than 50% of its O_3 would come from the New York City urban plume? This cannot be determined in any fixed manner, but a review of the results given by Cleveland et al. seems to indicate that the Hartford, Connecticut, area may be in the size range where 50% or less of its ozone problem can be due to advected O_3 (40). The 1970 population of the Hartford metropolitan area was about 700,000 with the city of Hartford having a population of about 160,000.

The question of upwind emission of O_3 precursors and the subsequent formation of photochemical O_3 over the downwind receptor area is another variation of O_3 advection. The separation of O_3 advection or transport from precursor advection is a difficult question to resolve. One way that could probably lead to a qualitative answer is the area-wide statistical analysis of O_3 data as done by Cleveland et al. The longer term relationships developed in such a study could show an O_3 pattern more closely linked to the large upwind urban area. Careful local studies of air chemistry could also be carried out such as was done by Westberg (37); however an unequivocal answer would be hard to obtain and expensive.

In situations where the upwind area is smaller than the receptor area, the evaluation of the impact on a larger population center in terms of either O_3 or precursors would be hard to measure to any degree of accuracy.

In all of these cases, calculated impacts derived from meteorological and chemical models can be obtained. The results would be questionable because, as yet, there are only crude photochemical models available. However, considering the problems that are encountered in field programs the modeled estimates may be as useful as any but the most comprehensive field study programs.

OZONE AND PRECURSOR TRANSPORT DISTANCES

Identifiable transport of O_3 over distances of 100 miles or more has been observed on a number of occasions, and the data reported by Siple et al. indicate that the New York City urban plume could be identified as an O_3 plume for 400 km (250 mi) out over the Atlantic (28). This is about a 24-hour or 1-day trajectory and may be about the limit for the identification of a particular plume. Beyond a 1-day transport distance, it would be expected that local meteorological conditions, such as turbulence and wind shear, would act to break up the identifiable plume; the pollutants it contained then would be more evenly mixed and included in the anthropogenic background levels. Cox et al. identified O_3 situations in England and southern Ireland that apparently had trajectories of over 600 km from European source areas (7).

In many situations an O_3 plume may persist in layers above the ground, but emissions of NO_x will completely scavenge the surface layers. This is commonly seen in city areas at night where O_3 will go to zero at the surface but may still be present aloft. This is a typical situation in southern California and was clearly observed over Canton, Ohio, by WSU in 1974. When this layer aloft is present at high concentrations, its mixing to the surface may make a major contribution to the next day's O_3 problem. These situations can be identified by field measurements using aircraft data taken during stable night and early morning hours. Fumigation situations might also be identified by a careful analysis of the O_3 time series and the local meteorology. It would probably be necessary to have such models verified by measurements aloft using aircraft.

The transport of O_3 precursors rather than O_3 doubtless occurs because O_3 seems to develop in the urban plumes downwind from the city. White et al. reported such an incident for the St. Louis plume (36). The unique identification of precursors in such plumes has generally been much less successful. Decker et al. tried to show NO_x buildup in the migratory anticyclones, but the levels were within the noise of their instruments (16). Detailed resolution of hydrocarbon species with regard to O_3 precursors also seems to be doubtful at this time. Thus the transport of O_3 precursors probably cannot be demonstrated at this time to occur over as long a distance as the transport of O_3 can be shown to exist. This may be more of an analytical problem than an indication that the phenomenon is not an important one.

CONTROL STRATEGIES RECOGNIZING OXIDANT TRANSPORT

Ozone or photochemical oxidant control strategies must be developed that take into account the extended transport that can occur between source areas and receptor regions. Thus the present concept that excessive concentrations at a given location must be countered by some control of emissions in the vicinity of the station must be expanded so that transport situations involving distant sources can be recognized and covered by special regulatory procedures. For example, it is obvious that O_3 concentrations along the Connecticut coast around Groton will never change significantly until the New

York City urban plume is reduced. Local control, even to the extent of moving the population out of the area, would probably not even be observable in local O_3 records. Other suburban areas in other parts of the U.S. could also be found where a similar situation prevails.

A control approach that seems reasonable to this investigator is one that is based first on control of the vehicle to the maximum practical extent without regard to its area of operation, and second the initiation of urban area vehicle travel control programs in selected major urban areas. The selection of those areas to be subject to area-wide transportation control plans would be based on two possible monitoring situations:

- The present concept of local adverse O_3 concentrations, but substantiated by good evidence that local sources are sufficient to produce the observed effect.
- The transport modified criteria where the relevance of upwind sources is judged and where meteorological and air chemistry data substantiate the regulatory decision. Here transportation control steps are prescribed in the upwind area rather than in the area where the excessive O_3 levels were measured.

There are many obvious problems in the implementation of such a control scheme, but compared to the inadequacies of the present system the usefulness of a change seems well worth the effort.

Probably one of the most serious regulatory problems is the adoption of apparently unnecessary controls. It seems that this problem would be less likely to occur in the scheme of regulations described above than under the present local control system. Where atmospheric transport is taken into account, agency control efforts could be concentrated in the larger and more congested urban centers, such as New York City, because these are the source areas that form significant urban plumes. This would seem to be a more publicly acceptable program.

REVIEW AND ANALYSIS

F.M. Vukovich

INTRODUCTION

The literature suggests that there are two predominant scales of transport that markedly affect the ozone concentration at the surface of the earth. These scales are: (a) the mesoscale transport that encompasses the effect of the urban heat island circulation, land and sea breeze circulations, and air pollution plumes downwind of major cities; and (b) synoptic-scale transport that appears to be closely associated with high pressure systems. These scales of transport do not designate necessarily the mechanism responsible for high ozone.

There is considerable controversy as to the principal mechanism responsible for levels of high ozone observed in locations remote from sources. Two conceptual models have been proposed. One suggests that direct transport of ozone is the principal mechanism. The ozone originates in urban areas or the stratosphere. The other model suggests that ozone precursors are transported to remote locations where they combine with naturally-emitted precursors to produce high ozone.

The credibility of these hypotheses is examined in this paper. The available information is employed to identify the strengths and weaknesses in each. From this analysis, a conclusion as to the dominant mechanism is suggested.

CHEMISTRY OF OZONE IN REMOTE REGIONS

Before considering oxidant transport, it is important to review recent

concepts on ozone chemistry in the rural environment. Recent outdoor smog chamber experiments by Sickles et al. indicate that in a partially spent simulated urban photochemical system, ozone was generated in concentrations above the NAAQS with low concentrations of NO and high NMHC/NO ratios (32). The smog chamber results indicate that dilution of the urban system results in more efficient generation of ozone per molecule of NO. It was further noted that at the end of a diurnal cycle a high minimum ozone concentration existed. These data strongly suggest that higher concentrations of ozone should be found in diluted plumes downwind of urban regions than in the urban regions. It will be shown later that this phenomenon is substantiated by observations in urban plumes.

The presence of large minimum concentrations in a dilute environment also suggests that the potential exists for producing high ozone concentrations on the following day without requiring either high generation or transport. This phenomenon will be substantiated.

Bufalini et al. have shown that all atmospheric organic compounds are capable of producing ozone (5). Larger molecules of organic compounds tend to produce larger concentrations of ozone. The reaction times of organic compounds in producing ozone vary substantially, ranging from a period for 99 percent reaction of one-half hour (trans-2-butene) to 150 days (methane). Most organic compounds have 99 percent reaction times of less than 12 hours. Carbon monoxide and acetylene have reaction times on the order of 8 1/2 days, whereas the reaction time of ethane is on the order of 4 days. These data suggest that the most reactive organic compounds are removed rapidly through ozone production. These reactions should take place either immediately at the source (e.g., the urban region) or immediately downwind of the source. The less reactive compounds would stay in the air parcel and accumulate. These would react at some later time (1, 2, or up to 8 days later). They could combine with more reactive compounds that may be injected into the system to produce high levels of ozone, particularly if a relatively high minimum concentration already exists.

Vukovich et al. have produced evidence that suggests that the less reactive hydrocarbons are important in producing high ozone levels (6). Data indicate that ozone concentrations began to decrease after a frontal passage, reaching a minimum somewhere between the frontal passage and the center of a following high pressure system. Following the ozone minimum, the ozone levels increase to a maximum on the back side of the high pressure system. Calculations show that on the front side of the high, an air parcel has been in the system usually less than a day. However, on the back side of the high, the air has been in the system for at least 2 and as many as 6 days. It is important to note that the high pressure system offers the proper environmental conditions (high solar radiation, low wind speed) for photochemical production of high ozone (2). The correlation between high air-parcel residence time and high ozone suggests that sufficient time exists for the less reactive hydrocarbons to accumulate and to react.

Vukovich et al. further showed that when high ozone is observed in a rural environment, it is usually in the presence of a high diurnal minimum from the previous day's diurnal cycle. These data showed that an extremely large generation or transport of ozone was not required to produce high ozone.

The conclusions of Vukovich et al. are in contrast to Lonneman's (47). Lonneman gave evidence that he said eliminated photochemical production of ozone in the rural environment as the mechanism for producing high ozone levels. He concluded that transport of ozone from upwind sources must be responsible for the high ozone levels. Lonneman cited measurements of ozone, hydrocarbon, and NO_x in the rural environment near Wilmington, Ohio, during August of 1974. Of the 14 observations presented, only six had diurnal maximum ozone concentrations (hourly average) greater than 80 ppb (the NAAQS). Using Dodges' model (48) and the observed NO_x and hydrocarbon concentrations, he showed that in only two of the cases were there sufficient NO_x and hydrocarbon to photochemically produce ozone concentrations greater than 80 ppb. His data indicate that in neither of these cases did the ozone actually exceed 80 ppb. It was on this basis that Lonneman concluded that photochemical production of ozone could not be responsible for the high ozone observed.

However, this fails to take into account the fact that, normally in rural areas, the nocturnal minimum ozone concentration is relatively large. For the summer of 1974, the average diurnal minimum at Wilmington, Ohio, was 20 ppb (2). Vukovich et al. have further shown that prior to the occurrence of high ozone in the rural environment, the diurnal minimum increases substantially. Therefore, it was only necessary that less than 60 ppb ozone be generated by photochemical processes to produce ozone greater than or equal to 80 ppb at Wilmington, Ohio. The data presented by Lonneman using Dodge's model suggests that 35 to 60 ppb ozone could have been generated easily by photochemical processes in the other cases.

Vukovich et al. show, using a simplified model, that synthesis and destruction of ozone are greater in the eastern part of the United States than in the western Great Plains region (6). This leads to the hypothesis that high ozone is correlated with high population density (16). The implication is, of course, that population density is proportional to the anthropogenic emissions of ozone precursors. The population density in the Great Plains area is on the order of 13 people per square mile, whereas, in the eastern part of the United States, it is on the order of 213 people per square mile. This hypothesis further suggests that each urban area, large or small, acts as a point source for ozone precursors. These are diluted in the air mass, but are sufficient for the genesis of high concentrations of ozone. The origin of the precursor in any single air parcel becomes obscure due to the scale of the transport. Though strong circumstantial evidence exists that supports this hypothesis (2,6,16,31,46), the results are not conclusive.

The above model implies that synthesis of ozone occurs in the rural boundary layer and that some of the precursors of ozone found in the rural boundary layer have urban origins. Although the evidence implies that this is the case, it is circumstantial. In the following section, further evidence to support this model is presented.

MESOSCALE TRANSPORT

There exists sufficient evidence to show that high ozone exists in plumes emitted from urban areas (38,49-51). These plumes extend anywhere from 60 to 3000 km downstream. In some cases such as the New York plume, large areas are affected. However, in most cases, such as the St. Louis plume, a very localized area downwind of the city is affected. Apparently, the affected area is a function of the area of the source (the area of the city).

An important point to note is that the maximum ozone level is found in the plume downwind of the city rather than in the city. Two potential processes may produce such a maximum. These are mass convergence and photochemical generation. Mass convergence requires some meteorological anomaly that would cause convergence of mass within the plume. Since the downwind maximum is found in all cases reported, this suggests that if it is a meteorological anomaly, the anomaly must be directly associated with the plume. However, there is no known forcing function associated with urban plumes that would cause a meteorological perturbation capable of producing mass convergence. It is therefore concluded that the principal mechanism for producing high ozone in the urban plume downwind of the city is photochemical generation. It is further suggested that the dilution effect discussed by Sickles et al. accounts for the downwind maximum (32).

Decker et al. have presented data from the DaVinci II experiment to show that during the daytime hours, the ozone is high both at the surface and aloft in the plume downwind of the city of St. Louis (9). However, at night the ozone concentrations aloft remain high, whereas the ozone concentrations at the surface diminish significantly. In the morning, the ozone aloft still is high, whereas the ozone at the surface begins to increase. Their observational period ended before the end of the diurnal cycle for the following day.

Based on these data, Ripperton et al. have established the following hypothesis (15). The high ozone observed during the day downwind of an urban region is a result of photochemical processes associated with precursors

transported in the urban plume. At night, a low level of inversion is developed by radiation processes. The inversion prevents mixing with the air aloft. Surface-based, ozone-destructive agents destroy the ozone trapped in the surface layer. Because mixing with the layers aloft is inhibited, ozone-destructive agents do not reach the air aloft, and the ozone there remains relatively unchanged. When, on the following day, solar insolation heats the surface layer, mixing brings considerable ozone to the surface. This hypothesis is supported by the observations of Coffey et al., Chatfield and Rasmussen, and Jerskey et al. (11,46,50).

The notion that vertical mixing of ozone is a principal mechanism leading to high ozone concentrations in the surface layer appears to be controversial, since much of the data that indicates mixing to be the principal cause for high ozone is from point observations. For instance, the data of Decker et al. consist of a point observation made aloft by DaVinci II and observations made at the surface by a mobile van. Coffey et al. report a point observation made at Whiteface Mountain that is compared to point measurements made at stations at lower levels, as far as 60 km from the Whiteface Mountain site (11). In none of these cases are there any real computations of vertical mixing, only the implication that since ozone is high aloft the flux must be downward and that this produces the observed high ozone at the surface later in the day.

This highlights an important shortcoming of ozone studies to date. There are no significant data on the diurnal variation of the vertical profile of ozone through the boundary layer. Only three such profiles have been reported (2,52).

These three profiles, though taken in different places, show similar diurnal variations. Before sunrise, relatively low concentrations of ozone are found in the surface layer compared to that aloft (see Figure 1). The concentrations of ozone aloft exceed the standards. At midday, the ozone concentration from the surface to the top of the boundary layer is approximately constant indicating a well-mixed boundary layer. In the late afternoon

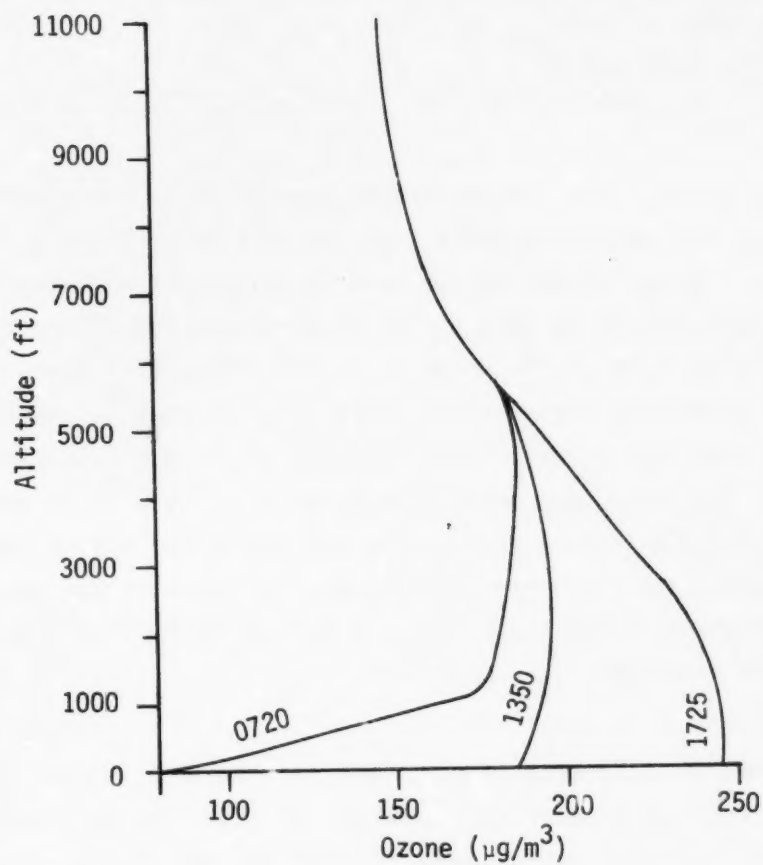


Figure 1. Diurnal variation of the vertical distribution of ozone at Wilmington, Ohio on 1 August 1974. These profiles have been smoothed using both the ascent and descent portions of aircraft flights where possible. The indicated times are the mean time (EDT) of each profile. Altitude is measured from the surface. (Unsmoothed data are in reference 2.)

around the time of maximum ozone at the surface, these profiles indicate that the ozone in the surface layer is significantly greater than the ozone aloft. The importance of this fact will be examined using Table 1.

TABLE 1. INTEGRATED AVERAGE OZONE CONCENTRATION FROM THE SURFACE TO 5,000 FT VERSUS TIME OF DAY USING DATA IN FIGURE 1.

Time (LDT)	0720	1350	1725
Average Ozone ($\mu\text{g m}^{-3}$)	155	185	225

The data in Table 1 show the integrated average ozone concentrations, where the integration was accomplished from the surface to 5,000 ft using the data in Figure 1. Mixing redistributes mass in a vertical column such that the resultant concentration of mass at any level within the column equals the average mass concentration in the column. In this particular case, the average mass concentration early in the morning is $155 \mu\text{g m}^{-3}$. Mixing could potentially increase the surface concentration from $80 \mu\text{g m}^{-3}$ (Figure 1) to $155 \mu\text{g m}^{-3}$ where the additional mass (approximately $75 \mu\text{g m}^{-3}$) is transported from layers above 1,000 ft to approximately the top of the mixing layer at 5,000 ft. If mixing alone produced the increase of ozone at the surface, then the mean concentration in the layer from the surface to 5,000 ft should have remained constant over time.

However, the data in the table show that, between 0720 LDT and 1350 LDT, there was an average increase of approximately $30 \mu\text{g m}^{-3}$ in the ozone concentration in the column. The total change of ozone at the surface in that time period was approximately $104 \mu\text{g m}^{-3}$ of which $75 \mu\text{g m}^{-3}$ or 72 percent of the change could have been accounted for by vertical mixing (but not necessarily). However, the total increase in ozone in the column in the time period relative to the profile one would get through mixing alone (i.e., a constant value of ozone at approximately $155 \mu\text{g m}^{-3}$ through the column) is a positive $185 \mu\text{g m}^{-3}$. Since mixing can only redistribute mass, it cannot account for this increase in mass in the column. Furthermore, it is noted between the time period 1350

LDT and 1725 LDT, that there was a further increase of approximately $45 \mu\text{g m}^{-3}$ in the column. A mass flux from the upper levels cannot be responsible for this mass increase since the gradient of ozone indicates that the flux should be from the surface to the upper levels.

These data suggest that, although, in the period after sunrise and before noon, the observed increase in ozone at the surface may be substantially influenced by vertical transport of ozone, there is a significantly more important process influencing the increase of ozone in the boundary layer.

Besides the urban plume, there are other mesoscale transport characteristics markedly affecting the ozone distribution. Hyde and Hawke discuss the occurrence of high ozone associated with morning drainage flow and afternoon sea breezes (20). They indicated that drainage flow brings precursors of ozone from inland sources to the Sydney basin, and that the sea breeze brings pollution air (in which significant photochemical processes have occurred) back to the Sydney basin in the afternoon.

Kauper and Niemann discuss the influence of the upper-level flow associated with the Los Angeles land breeze on the transport of high ozone to Ventura County (18). They indicated that ozone-rich layers exist aloft over Los Angeles, and that these are transported by the land breeze to Ventura County where mixing brings the aged photochemical pollution cloud to the surface. The authors do not offer concrete evidence that the air pollution aloft comes to the surface in Ventura County. They only suggest this as a possible mechanism for the high ozone in Ventura County. The conclusion that the upper-level land breeze influenced the horizontal transport of ozone aloft, however, was well substantiated.

Decker et al. studied the relationship of transport to high ozone observations in the gulf coast regions of the United States (16). The study was concentrated in the two-state area of Louisiana and Texas. On this scale, it was found that the higher concentrations of ozone were associated with slow-moving air that passed over high precursor emission areas and arrived from a non-prevailing wind direction. The lower concentrations were associated with

faster-moving air having a long fetch over water. In those cases where high ozone was associated with flow from the Gulf of Mexico, it was found that the air had a previous history over the high precursor emission regions of Louisiana and Texas (southerly flow) and that changes in wind direction (northerly flow) brought this air back to the coast. Though the evidence is far from being conclusive, it indicates that, on the average, air parcels from the source region of the Gulf of Mexico contained low concentrations of ozone. This is important because it infers that oceanic areas are sinks for ozone.

SYNOPTIC-SCALE TRANSPORT OF OZONE

Considerable evidence exists in the literature relating high ozone and synoptic-scale high pressure systems (6,11,12,14,15,16,31,46). There is also substantial evidence that the high ozone is found on the western side (back side) of an eastward moving high pressure system. Though the relationship between high ozone and high pressure appears to be well substantiated, there exists considerable controversy as to the mechanism that produces the high ozone in the high pressure system. Three mechanisms are discussed in the literature. These are: (a) the direct transport of ozone; (b) the direct transport of ozone precursors from the southern portions of the high pressure system and subsequent photochemical production; and (c) the synthesis of high ozone in air parcels that have large residence times in the high pressure system. Though the last two appear to be similar (i.e., the mechanism is synthesis), there is a fundamental difference between the basic characteristics (the transport) of the system that allows the synthesis of ozone.

The conclusions reached by Coffey et al. and Dobbins et al. support the notion that direct transport, either vertically or horizontally, of ozone is a principal mechanism producing high ozone over a large area (11,17). Both investigators suggested that above the nocturnal inversion, high ozone persists throughout the night and serves to replenish the surface ozone concentration during the daylight hours. The mechanism was discussed in some detail in the previous section; however, there are further aspects concerning that question.

Both of the investigators conclude that vertical mixing is the primary mechanism for producing high ozone at the surface. If this is true, then one must ask why is high ozone associated with high pressure systems (a point that Coffey et al. also noted). More significant vertical mixing occurs in low pressure systems, yet no statistical correlation has been found between high ozone and low pressure systems. Admittedly, cases of high ozone in low pressure systems have been found, but these have been isolated cases.

Potential sources of ozone are the stratosphere and urban regions. Transport of ozone from the stratosphere could be a mechanism for high ozone at the surface. Reiter has shown that downward transport of ozone from the lower stratosphere accompanies tropopause folding (53). Evidence exists that in the springtime there is increased transport of ozone from the stratosphere to troposphere (43,52). Though these data suggest the potential for ozone from the stratosphere to contribute to the ozone found at the surface, there is no concrete evidence to date that demonstrates that this ozone is responsible for the large summertime high ozone concentrations found at the surface. Furthermore, many of the more recent vertical profiles of ozone through the troposphere in high ozone situations indicate the presence of a minimum concentration for ozone in the midtroposphere with ozone increasing above and below that point reaching a maximum in the stratosphere and near or at the surface (Figure 2). This suggests two distinct regions of ozone activity: the upper layer having its source in the stratosphere, and the lower layer having its source at the surface. This further indicates that the high ozone in the lower troposphere is the result of some mechanism other than transport of ozone from the stratosphere.

Sufficient data exist that show a preference for high ozone to occur on the back side of a migratory high pressure system. In the high pressure systems, mixing through a deep portion of the atmosphere is severely inhibited by the presence of a subsidence inversion (12). It may be that the subsidence inversion is responsible for the local minimum at midtroposphere in vertical profiles of ozone in high ozone conditions.

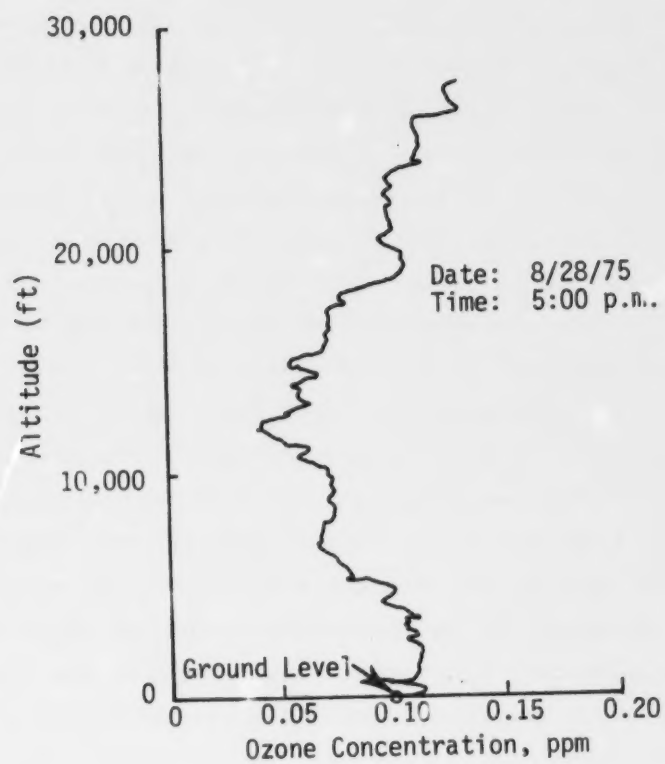


Figure 2. The vertical distribution of ozone over Indianapolis (52).

Coffey et al. pointed out that urban areas have less ozone than rural areas (11). This factor was also pointed out by Ripperton et al., who used it to show that it is unlikely that direct transport of ozone from urban areas to rural areas is the principal mechanism producing high ozone in rural areas on a synoptic scale (15). If the urban region were the source of ozone and direct transport were the mechanism, there could not be higher ozone in the rural areas than in the urban areas. This is because the urban areas constitute about one-fourth the volume of the United States air mass (the urban area multiplied by the height of the daytime boundary layer) compared with three-fourths for the rural area. Thus, volumetric mixing would yield smaller concentrations of ozone in rural regions than in urban regions. Since available evidence indicates that rural regions have, on the average, larger concentrations of ozone than urban regions, this signifies that another mechanism prevails.

Wolff et al. and Shenfield indicate that synthesis of ozone is most probably the mechanism that produces high ozone on a synoptic scale in the rural boundary layer (14,54). High ozone is concentrated on the back side of the high where the flow is generally from the south to the north. This suggested that there is generally transport of ozone precursors from the south to the north part of the back side of the high where the high ozone is produced. The fact that long distance transport (≥ 1000 km) of ozone precursors occurs has been discussed by Cox et al. and Grennfelt (7,21). Flow from the southern portions of a high pressure system to the northern portions of a high pressure system on the back side only occurs when that high pressure system is stationary. Under such conditions, it has been shown that high ozone is concentrated over most of the area encompassed by the high pressure system. Under these conditions, the highest ozone has been found to be located around the center of the high pressure system where transport is minimized (2). Theoretical calculations in moving high pressure systems have suggested that the motion of an air parcel through a moving high pressure system is basically from the west through the east (9). For a high pressure system moving at 10 meters per second, the total travel distance of an air parcel in the high pressure system will be about 350 nautical miles. About 60 percent of that

travel distance will be in a west to east direction. Long-distance transport (distances much greater than 1,000 km) in a south to north or north to south direction does not occur in most of the moving high pressure systems.

As pointed out earlier, Vukovich et al. have shown a correlation between the residence time of air parcels and high ozone in moving high pressure systems (6). In such systems, high residence time and high ozone are both found on the back side of a high pressure system. It was found that the source region of air with large residence times was the northeastern quadrant of the high pressure system. The data also suggest that vertical transport of ozone is not responsible for the high ozone. Therefore, photochemical generation is concluded to be the principal mechanism.

The fact that the high residence time and high ozone correlated suggests that a period of time is required so that sufficient or critical concentrations of ozone precursors are injected into the air parcels while they remain in the high pressure system where proper environmental conditions exist for ozone production (i.e., high solar radiation, low wind speed). Decker et al. have inferred that it is the less reactive hydrocarbons that accumulate or reach critical concentrations (9). After a certain time, these begin to react and produce ozone. This mechanism is augmented by daily injection of the very reactive hydrocarbons from anthropogenic and natural sources to produce the high ozone in the rural boundary layer.

Decker et al. have also shown that, in the regions from the Rocky Mountains to the east coast of the United States, there exists a gradient of ozone such that the ozone is low in the west and high in the east (9). Furthermore, Vukovich et al. have shown that, as a high pressure system moves out of Canada to the western portions of the above-mentioned regions and, subsequently, to the eastern portion of that region, the ozone concentrations in the high pressure system were larger when the system was in the east (6). Sandhu has shown that $20 \text{ to } 60 \mu\text{g m}^{-3}$ is a typical background concentration for ozone in the rural Alberta, Canada, environment (55). Alberta is a major source region for continental high pressure systems that move into the United States east of the Rocky Mountains. In the eastern portions of the United States, ozone

concentrations in the high pressure system exceed the United States standards for ozone. It was further shown that, though the ozone was higher in the east than in the west and both photochemical production and destruction are larger in the east than in the west in these migratory high pressure systems, the amplitude of ozone (the maximum concentration of ozone minus the minimum concentration of ozone) was not significantly different in the east from that in the west. The real difference was in the minimum concentration for ozone. In the east, the minimum concentration was three times greater than that in the west. These factors have led Decker et al. and Ripperton et al. to conclude that high ozone is related to high population density, which, of course, is related to high anthropogenic emissions of ozone precursors (15,16).

Husar et al. noted a correlation between elevated ozone concentrations and atmospheric visibility or haziness (13). A similar correlation was found with high levels of sulfate. This is an important finding in that it suggests a correlation between atmospheric haziness and air pollution, not specifically ozone, which may define the dimensions of the problem. Though the correlation seems to exist, the significance of the correlation is somewhat masked by the fact that the visibility observations were made using data from NOAA weather stations. These are normally located in major urban areas. It is impossible to determine what effects local perturbations produced by the urban air pollution had on the visibility relative to the interpolation of the analyses into rural regions. Husar et al. imply that the synoptic-scale zone of haziness moves with the air mass, which then suggests the air pollutants move with the air mass. The haziness was associated with a high pressure system in the east. These systems move as a result of changes in the columnar divergence, whereas haziness that is a result of suspended aerosols must move with the wind. These movements are normally independent of each other. It is suggested that the changes in haziness may be the result of the formation of haze and the dilution of aerosols.

SUMMARY AND CONCLUSIONS

There are two major scales of transport related to high surface ozone concentrations: mesoscale transport and synoptic-scale transport. On the mesoscale, the urban plume is most significant. The nature and scale of the urban plume is dependent on the nature and scale of the source, i.e., the urban area. Assuredly, direct transport of ozone occurs in the urban plume. However, the fact that the observations show that there is a maximum ozone concentration downwind of the urban region indicates that photochemical production of ozone must occur since a meteorologically-induced mass convergence is unlikely. The photochemical production is most probably a result of downwind transport of ozone precursors in the urban plume, combined with the effect of dilution on the ozone chemistry.

Widespread regions of high ozone are found in the rural boundary layer associated with migratory high pressure systems. The high ozone is generally found on the back side of the high and only when the high pressure system is in the eastern portions of the United States. Available vertical profiles through the troposphere show that when the ozone is high at the surface, a minimum ozone concentration is found in the mid-troposphere. This suggests strongly that there are two regimes of ozone behavior: that above the minimum which is dominated by the stratosphere; and that below the minimum which seems to be dominated by activity at the surface. Though existing vertical profiles through the boundary layer suggest that mixing may be important in the morning immediately after sunrise, they show that mixing is not the predominant mechanism producing diurnal variations of ozone at the surface.

Comparisons of rural and urban data show that on the average the rural ozone concentrations are larger than the urban concentrations. This factor, plus the fact that volumetric dilution would produce the opposite effect, indicates that direct transport of ozone from urban sources is not responsible for the widespread high ozone episodes found in the rural boundary layer.

By process of elimination based on existing evidence, this leaves photochemical generation as the remaining mechanism that could be responsible for

the high ozone in the rural boundary layer. It is suggested that the urban mix of very reactive and less reactive ozone precursors is transported into the rural boundary layer. The very reactive precursors produce ozone immediately. This accounts for the downwind high ozone in urban plumes. The less reactive precursors remain in the air parcel. The air parcel continues its motion collecting very reactive and less reactive anthropogenic and natural ozone precursors in its traverse through the boundary layer. Daily, it loses the very reactive precursors, but increases the concentration of the less reactive precursors. Finally, with sufficient sunlight, less reactive precursors begin to produce ozone. This, combined with the production from more reactive precursors collected daily, allows the air parcel to contain large concentrations of ozone.

Sufficient sunlight is available in the relatively cloud-free high pressure systems. Evidently, it takes somewhere between 2 and 6 days for the less reactive precursors to become active according to theoretical computations of air parcel residence times in high pressure systems. This is consistent with chemical evidence. At the time high ozone occurs in the air parcels, identification of specific sources that have contributed to the ozone precursor concentration is not possible. The transport of precursors in this case is on the order of 1000 km or greater.

The basic conclusion of this analysis is that the most important mechanism for producing high ozone in the rural boundary layer on any scale is the transport of ozone precursors from anthropogenic and natural sources combined with photochemical generation. This factor is most important on the synoptic scale in the eastern portions of the United States and on the mesoscale immediately downwind of any urban area.

RECOMMENDATIONS FOR FURTHER RESEARCH

There are two major areas where additional data are required to remove uncertainties in the model. First, additional measurements are needed to understand the role of mixing in the boundary layer on the diurnal variation

of ozone, particularly under high ozone conditions. This would require that vertical profiles of ozone be obtained diurnally through the boundary layer with both high and low ozone concentrations at the surface. This study should be conducted in a number of locations in the continental United States. Each measurement series should extend over a 4- to 6-week period. Measurements should include vertical profiles of wind and temperature through the boundary layer, which are useful in computations of mixing.

The second study needed involves the transport of ozone from the stratosphere to the surface and the relationship of that transport to high ozone episodes. In this case, daily vertical profiles of ozone through the troposphere would be the data base. Along with these data, basic meteorological information should be obtained through the troposphere. The profiles should be obtained during the time that the diurnal maximum at the surface is reached. This study should be undertaken in a 3- to 4-month period, encompassing mid-spring to midsummer. During that period, special diurnal vertical profiles through the troposphere should also be obtained for very specific situations (e.g., during periods of tropopause folding).

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